Di-*tert*-butyl nitroxide is a free-radical inhibitor[5] and *m*-dinitrobenzene is generally regarded as a scavenger for radical anions.[5] These facts strongly support our contention that the reaction in eq 2 is an electron-transfer chain process.[6,7]

In accord with the proposed mechanism the transformation of eq 2 is induced by electron donors and by free radicals. Thus, although there is no detectable reaction in DMF in the dark at room temperature after 24 h, in the presence of $Na_2S_2O_4$ (3 equiv) none of the nitro compound (**2**) remains after 24 h in the dark at room temperature and a 40% yield of the pure product (**3**) is isolated (65% yield by GLC).[8] Furthermore, in the presence of 8 mol % of di-*tert*-butyl peroxyoxalate[9] the reaction of eq 2 proceeds 61% to completion in the dark in 24 h at room temperature and a 40% yield of pure **3** is isolated. Azobisisobutyronitrile also induces the reaction of eq 2 at 80 °C in the dark; a 50% yield (by GLC) of **3** is obtained after 3 h in the presence of 10 mol % of azobisisobutyronitrile. In the absence of the azo compound a 10% yield of **3** is obtained. This ability of free radicals to induce an electron-transfer chain process is especially noteworthy and should prove of wide applicability.

The experimental procedure for these reduction is illustrated by the reduction of eq 2. A mixture of **2** (1.84 g, 10 mmol) and **1** (6.42 g, 30 mmol) in benzene (150 mL) was stirred for 24 h at room temperature under nitrogen with exposure to a 150-W tungsten lamp. The resulting mixture was washed with 2 N HCl and then with water. The benzene layer was dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation gave 0.82 g (60% yield) of pure **3**, bp 96 °C (2.8 mmHg).

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(1) T. C. Bruice and S. T. Benkovic, "Bioorganic Mechanism", Vol. 2, Benjamin, New York, 1966, and references cited in recent reports. See D. M. Hedstrand, W. M. Kruizinga, and R. M. Kellogg, *Tetrahedron Lett.*, 1255 (1978).

(2) H. Sund in "Biological Oxidation", T. P. Singer, Ed., Wiley-Interscience, Robinson, New York, 1968, pp 621–624. J. J. Steffens and D. M. Chipman, *J. Am. Chem. Soc.*, **93**, 6694 (1971), and references cited therein. Nonchain free-radical mechanisms have been proposed for the reduction of thiobenzophenone by BNAH [A. Ohno and N. Kito, *Chem. Lett.*, 369 (1972)] and for the replacement of the bromine atom of α-bromonitro compounds by BNAH [R. J. Kill and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 755 (1976)]. However, a recent paper by R. A. Hood, R. H. Prince, and K. A. Rubinson [*ibid.*, 300 (1978)] claims that the detection of free radicals in these reductions by ESR is due to artifacts.

(3) Two other methods for replacing the nitro group by hydrogen have recently been described: the use of the sodium salt of methyl mercaptan at 25 °C [N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **101**, 647 (1979)] and treatment with KOH in ethylene glycol at 120–140 °C [A. L. Krasuska, H. Piotrowska, and T. Urbanski, *Tetrahedron Lett.*, 1243 (1979)].

(4) Thus, a preliminary attempt to replace the nitro group of compound **2** by hydrogen using $CH_3S^-Na^+$ yielded no product; this may be a consequence of a reverse Michael reaction. Compounds which can be reduced by BNAH are usually more conveniently reduced by other hydride transfer agents such as sodium borohydride, but, with compounds listed in Table I which contain the specified α-nitro group as well as borohydride-reducible groups, BNAH selectively replaces the nitro group by hydrogen without affecting the other functions, while sodium borohydride selectively reduces the borohydride-reducible groups (e.g., keto) without affecting the nitro group. This may be the first case in which BNAH reduces a substrate which is inert to sodium borohydride.

(5) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **15**, 734 (1975).

(6) Analogous results using 20 mol % of di-*tert*-butyl nitroxide and 10 mol % of *m*-dinitrobenzene have been obtained for the reaction of entry 5 in Table I.

(7) Apropos of the inhibition of *m*-dinitrobenzene, failure of the reaction of entry 8 (Table I) reasonably reflects similar inhibition associated with this substrate's *p*-nitrobenzoyl moiety itself.

(8) $Na_2S_2O_4$ is known to be a one-electron-transfer agent; see, for example, P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1136 (1964). It is not clear how much of added $Na_2S_2O_4$ is used to induce this reaction, for $Na_2S_2O_4$ is only slightly soluble in DMF. However, **2** is not converted into **3** on treatment with $Na_2S_2O_4$ in the absence of BNAH.

(9) P. D. Bartlett, E. P. Bezing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

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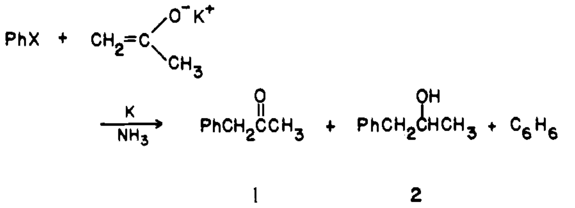
A Major Leaving Group Effect on Chemical Events after the Group Has Left: Reactions of Acetone Enolate Ion with Halobenzenes and Related Substrates Provoked by Solvated Electrons

Sir:

The phenyl halides and like substrates react with potassium acetone enolate and solutions of potassium metal in ammonia to form phenylacetone (**1**), 1-phenyl-2-propanol (**2**), and benzene[1] (eq P1). The proportions depend strongly on the leaving group, as reported in Table I. For example, the ketone/alcohol (**1/2**) product ratio is ~7 from PhI but only ~0.6 from PhCl. The proportion of benzene generally is higher when the ketone/alcohol ratio is smaller.



$$PhX + CH_2{=}C(O^-K^+)CH_3 \xrightarrow[NH_3]{K} PhCH_2\overset{O}{\overset{\|}{C}}CH_3 + PhCH_2\overset{OH}{\overset{|}{C}}HCH_3 + C_6H_6 \quad (P1)$$

These reactions are believed to occur according to the mechanism sketched in Chart I. This is an elaborated $S_{RN}1$ mechanism;[2] step 1 effects initiation, steps 2, 3, and 4 constitute a propagation cycle, steps 6 and 8 are termination steps, steps 5, 7, and 9 are proton transfers, and step 10 is a familiar type of electron transfer. According to this mechanism, the relative yields of products **1** and **2** are determined primarily by the extents to which steps 4 and 8 are utilized.

It is noteworthy that the leaving group is present in the reactants for steps 4 and 8 only in the electron-accepting ArX for step 4. In an earlier report,[1] it was postulated that the leaving group influences product composition by its effect on the rate of electron transfer from **3** in step 4. We shall present evidence that such is not the case, and therefore that *the leaving group exerts a strong influence on chemical events that occur after its departure from the reacting species.*

The following facts are relevant. (a) Whereas early data[1] afforded a strictly linear plot of log (**1/2**) for each halobenzene against the logarithm of the rate constant for its reaction with

Chart I

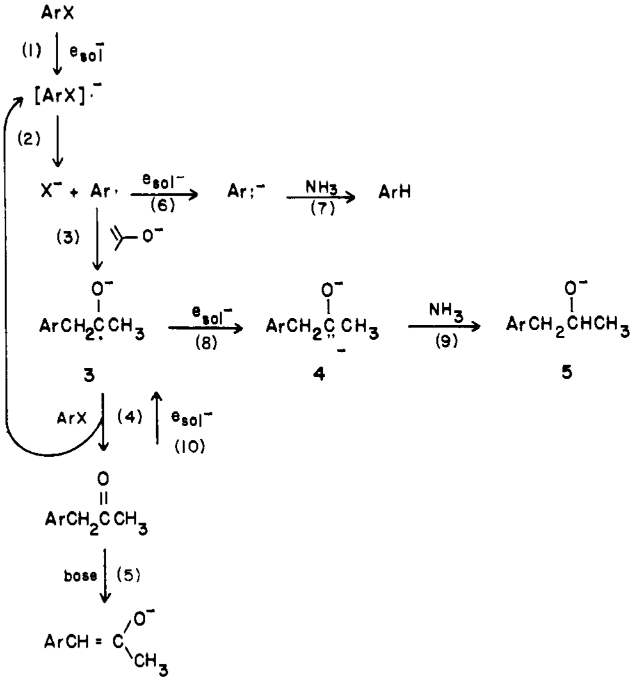


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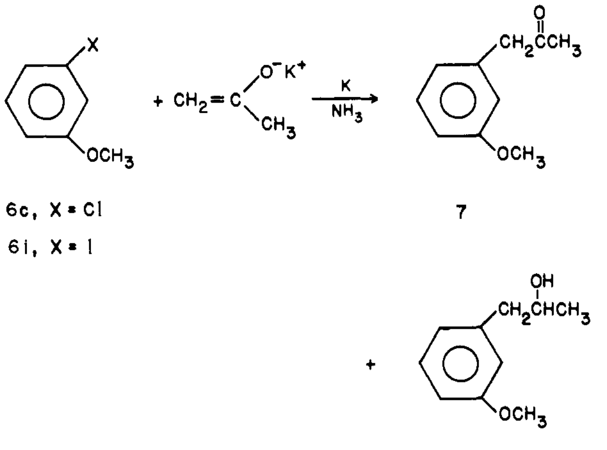
Table I. Reactions of Phenyl Halides and Related Substrates with Potassium Acetone Enolate and Potassium[a] in Ammonia at −33 °C

expt	substrate (ArX)	NH_3, mL	recovered ArX, %	X^-, %	mol of K/mol, of ArX[b]	product yields,[c] % ArH	1 or 7	2 or 8	1/2 or 7/8
1	PhI	500	0	99	0.73	4	65	10	6.6[d]
2	PhBr	100	0	*e*	1.38	6	78	11	7.0
3	PhCl	500	15	82	1.43	18	20	37	0.55[f]
4	PhF	100	*e*	*e*	1.72	29	12	42	0.28
5	$PhNMe_3^+I^-$	100	*e*	*e*	1.23	12	54	20	2.7
6	Ph_2O	500	0	*e*	1.83	41	7	28	0.25
7	Ph_2S	100	0	*e*	1.39	17	30	34	0.88
8	Ph_2Se	500[g]	0	*e*	1.73	25	21	25	0.83
9	**6i**	50	0	98	0.68	4	54	8	6.9
10	**6c**	50	66	34	0.49 (1.43)	9	6	12	0.51
11	PhI	50	9	89	0.77 (0.90)	6	76	3	23
	6c		15	84		13	20	31	0.64
12	PhCl	50	26	74	0.68 (0.81)	15	20	43	0.47
	6i		19	79		5	53	2	28
13	**6i**[h]	50	0	96	0.67	11	54[i]	4	13
14	**6c**[j]	50	34	66	0.90 (1.36)	21	9[k]	21	0.45
15	C_6D_5Cl	100	0	*e*	excess	*e*	*e*	*e*	0.64
16	PhI	100	0	*e*	1.55	19[l]	43.3[m]	26.7[n]	20
	C_6D_5Cl		0	*e*					0.38

[a] Bits of K metal added to 9 mmol of total substrate dissolved in ammonia containing 27 mmol of potassium acetone enolate (from KNH_2 and acetone at −78 °C) and 9 mmol $Me_3CO^-K^+$. [b] In parentheses, moles of K per mole of ArX consumed. [c] Determined by GLC. [d] In other experiments, the ratio of **1**/**2** from PhI varied from 1.1 to 5.9. [e] Not determined. [f] In other experiments, the ratio of **1**/**2** from PhCl varied from 0.21 to 0.42. [g] Solvent contained 4% tetrahydrofuran. [h] **2** (4.5 mmol) was also present. [i] **1** (7% on basis of **6i** supplied) was also formed. [j] **2** (3.6 mmol) was also present. [k] **1** (2% on basis of **6c** supplied) was also formed. [l] By MS, the ratio of C_6HD_5 to C_6H_6 was 1.92. [m] By MS, the ratio of $C_6D_5CH_2COCH_3$ to **1** was 0.281. [n] By MS, the ratio of $C_6D_5CH_2CH(OH)CH_3$ to **2** was 14.7.

the solvated electron in water,[3] more extensive data confirm the trend but do not afford precisely linear plots. (b) The observed product ratios from identical reactants vary somewhat from experiment to experiment, even when efforts are made to maintain uniformity of procedure. (c) Drastic changes in procedure only modestly affect the product ratios; thus similar trends were observed when bits of potassium metal were added to solutions of PhX with fourfold excess of the enolate reagent (prepared from acetone and KNH_2) until a blue color persisted, or when PhX was added to a solution of the enolate and insufficient potassium for complete reaction, or when PhX was added to a solution of the enolate and excess potassium so that the mixture was blue at the end of the process. (d) A *m*-methoxy group has little effect on the ketone/alcohol product ratio; thus the **7**/**8** ratio from **6i** (eq P2) is 6.9 (expt 9, Table I), whereas from **6c** it is 0.51 (expt 10). (e) Pentadeuteriochlorobenzene behaves much as does chlorobenzene (expt 15). (f) When 1-phenyl-2-propoxide ion (from **2**) was present during reactions involving **6i** and **6c**, very little oxidation to **1** occurred (expt 13 and 14). Some abstraction of α-H from the alkoxide ion by aryl radicals,[4] to form a radical anion of type **3** which then progresses in part to an arylacetone, appears to occur as a minor feature of the system.



6c, X = Cl
6i, X = I
7
8 (P2)

Two other kinds of fact strongly guide interpretation. One is that, when pairs of PhX (e.g., PhI and PhCl) with a slight excess of *tert*-butyl alcohol are treated with a deficiency of potassium metal, added either as bits or as a dilute solution in ammonia, they show equal reactivity; that is, the amount of each halide ion released is proportional only to the original concentration of the respective PhX. This *macroscopic* effect is indicative of control of *macroscopic* reaction rate by mixing. Each PhX reacts sufficiently fast with the solvated electron so that it reacts if the volume element in which it exists happens to be mixed with solvated electrons but not if it is not mixed.

The other is that a mixture of PhI and **6c**, or of PhCl and **6i**, gives for each aryl group a ketone/alcohol ratio characteristic of the halogen originally present. Indeed, differences in product ratios are accentuated in such experiments. Thus, in expt 11 a mixture of PhI and **6c** gave product ratios of **1**/**2** of 23, and of **7**/**8** of 0.64, while in expt 12 a mixture of PhCl and **6i** gave ratios of 0.47 and 28, respectively. Likewise, in expt 16 a mixture of PhI and C_6D_5Cl gave a **1**/**2** ratio of 20 and a $C_6D_5CH_2COCH_3/C_6D_5CH_2CH(OH)CH_3$ ratio of 0.38. These experiments exclude the possibility that product ratios are primarily determined by rates of electron transfer in step 4, as earlier proposed.[1] Though we grant that, in step 4, PhI or **6i** probably accepts electrons faster than does PhCl, **6c**, or C_6D_5Cl, this increased reactivity should be available in expt 11, 12, or 16 to any of the species of type **3**, regardless of the halogen originally present. If there were competition between steps 4 and 8 in homogeneous solution, the arylacetone/1-aryl-2-propanol product ratios in these mixed experiments should be of similar magnitude for the phenyl, pentadeuteriophenyl, and *m*-methoxyphenyl products.

Despite the aforementioned evidence that reactions of solvated electrons with halobenzenes occur during mixing, we considered two other models of reaction in homogeneous solution. One model postulated (i) that ArX reacts with the enolate ion to form arylacetone, (ii) that $[ArX]^-\cdot$ reacts with the enolate ion to form a radical anion of type **3** which is further transformed into alkoxide ion **5**, and (iii) that ArX and $[ArX]^-\cdot$ might exist in equilibrium dependent on the identity of X. The other model postulated that two different electronic states of aryl radicals were formed in fragmentation step 2, in proportions depending on the identity of X, and that one type of state yielded ultimately arylacetone and the other type 1-aryl-2-propanol. Both these models were dismissed for reasons that will be argued in later full publication.

One model of reaction during mixing fails to accommodate the data. According to it, an electron-rich zone of solution, which may contain enolate ions but no aryl halide molecules, advances smoothly in the manner of a phalanx into an "electronless" zone containing both aryl halide and enolate species. A particular aryl halide molecule is suddenly surrounded by solvated electrons, and thereafter it and any species derived from it exist in an electron-rich environment. On this model, PhI and PhCl should give identical product proportions, and indeed both would give mainly benzene inasmuch as the aryl radical should react faster with the solvated electron (step 6) than with the enolate ion (step 3) when both are present in substantial concentration.

A second mixing model provides useful insight. It is one of ragged advance, in which raiding parties of solvated electrons sortie into the "electronless" zone and are annihilated upon encountering aryl halide molecules (step 1). The resulting $[ArX]^{-}\cdot$'s, being momentarily in an "electronless" zone, have an opportunity to undergo the sequence of steps 2–5 to form the enolate ion of the arylacetone product.[5] Fragmentation step 2 is much faster for $[ArI]^{-}\cdot$ than for the corresponding $[ArCl]^{-}\cdot$,[6] and therefore the several intermediates derived from ArI have a better change of completing steps 2–5 before the main force of solvated electrons arrives. When the main force arrives, steps 6 and 8 rapidly occur and dominate product formation. One thus interprets a strong leaving group effect on product composition in terms of a *microscopic* effect, namely, competition between rate of electron advance and rate of fragmentation of $[ArX]^{-}\cdot$, the latter known to depend on the identity of X.[7]

However, this model gives no interpretation of why an aryl chloride serves to increase the ketone/alcohol product ratio from an aryl iodide also present. We suggest that ArCl-derived intermediates (aryl radicals and radical anions of type **3**), which remain after most of the corresponding ArI-derived species have reacted, may combine sacrificially with an ensuing surge of solvated electrons so as to protect the ArI-derived intermediates from assault. This could happen only if the two series of reacting intermediates were spatially separated, with the ArCl-derived species closer to the front of advancing solvated electrons and the ArI-derived species deeper within the "electronless" zone. That state of affairs might develop if at least part of the electron advance were by tunneling, and if electrons could tunnel farther to get to ArI molecules than to aryl radicals or radical anions of type **3**. In that case electrons could tunnel through a thin reaction zone, populated largely by ArCl-derived intermediates, to ArI molecules farther from the front where the latter could then react behind a protective screen of ArCl-derived intermediates.

Much of the migration of solvated electrons is believed to occur by tunneling,[10] and there is evidence that electrons can tunnel farther to PhI than to PhCl molecules.[11-13] Plausibly their ability to tunnel to Ar· or **3** species is limited to even shorter distances.

Clearly both the experimental phenomenon that we describe and the interpretations that we offer call for further attention. Nevertheless, it is evident that, when reaction occurs during mixing, the product formed from a reactive intermediate may depend not only on what it is, but on where and when it is formed.

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(3) Anbar, M.; Hart, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5633.

(4) Boyle, W. J., Jr.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 1418.

(5) We have shown experimentally that the enolate ion of **1** is little affected by excess solvated electrons.

(6) Alwair, K.; Grimshaw, J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1811. Nelson, R. F.; Carpenter, A. K.; Seo, E. T. *J. Electrochem. Soc.* **1973**, *120*, 206. See also: Saveant, J.-M.; Thiebault, A. *J. Electroanal. Chem.* **1978**, *89*, 335. Amatore, C.; Chaussard, J.; Pinson, J.; Saveant, J.-M.; Thiebault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.

(7) If fragmentation of $[ArX]^{-}\cdot$ were very slow, it might be surrounded by solvated electrons before it fragmented. In that case steps 6 and 7 forming benzene or derivative thereof may well predominate, and no arylacetone or 1-aryl-2-propanol may be formed.[8] This constitutes an alternative interpretation for an earlier observation[9] that, whereas many PhX's react with acetone enolate ion and potassium according to eq P1, others are cleaved to form benzene without **1** or **2**.

(8) Cf. Bunnett, J. F.; Gloor, B. F. *Heterocycles* **1976**, *5*, 377.

(9) Rossi, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 112.

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(12) In separate reactions, deeper tunneling to PhI than to PhCl would also contribute to enhancement of the **1**/**2** ratio from PhI over PhCl.

(13) The concept of electron transfer at a greater distance to iodine than to chlorine compounds provides an alternative interpretation for the fact[14] that in reactions of alkyl halides with disodium tetraphenylethylene the yields of reduction products (as contrasted to products of alkylation of tetraphenylethylene) decrease in the order RI > RBr > RCl. On this concept, the alkyl radical formed immediately after electron transfer to an alkyl iodide, compared with an alkyl bromide or chloride, is farther from the byproduct tetraphenylethylene radical anion and, so to speak, has a head start on getting away from it.

(14) Garst, J. F.; Roberts, R. D.; Pacifici, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3528.

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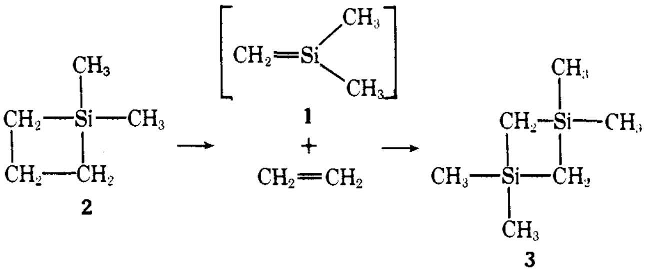
An Electron Diffraction Study of 1,1-Dimethylsilaethylene

Sir:

Although attempts to synthesize stable molecules containing carbon–silicon double bonds date back to nearly the turn of the century,[1] all efforts have been unsuccessful. In 1966 Gusel'nikov provided a number of lines of indirect evidence that 1,1-dimethylsilaethylene (DMSE, **1**) is a short-lived intermediate in the thermolysis of 1,1-dimethylsilacyclobutane (DMSCB, **2**), yielding 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB, **3**) and ethylene.[1,2] Subsequently, intermediates possessing carbon–silicon double bonds have been postulated in a variety of retrocycloadditions, thermal and photochemical rearrangements, and elimination reactions.[1] Theoretical discussions of the structure, stability, and lack of persistence of silaalkenes abound.[3] Several spectroscopic investigations of silaalkenes have been published.[4,5] We report herein the first structural study of a molecule containing a carbon–silicon double bond, a gas-phase electron diffraction study of DMSE (**1**).



DMSE was generated by the pyrolysis of DMSCB. Gen-